

Airborne measurements of carbonaceous aerosol soluble in water over northeastern United States: Method development and an investigation into water-soluble organic carbon sources

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[1] A particle-into-liquid sampler (PILS) was coupled to a total organic carbon (TOC) analyzer for 3 s integrated measurements of water-soluble organic carbon (WSOC) in PM₁ ambient particles. The components of the instrument are described in detail. The PILS-TOC was deployed on the NOAA WP-3D aircraft during the NEAQS/ITCT 2004 program to investigate WSOC sources over the northeastern United States and Canada. Two main sources were identified: biomass burning emissions from fires in Alaska and northwestern Canada and emissions emanating from urban centers. Biomass burning WSOC was correlated with carbon monoxide (CO) and acetonitrile ($r^2 > 0.88$). These plumes were intercepted in layers at altitudes between 3 and 4 km and contained the highest fine particle volume and WSOC concentrations of the mission. Apart from the biomass burning influence, the lowest WSOC concentrations were recorded in rural air masses that included regions of significant biogenic emissions. Highest concentrations were at low altitudes in distinct plumes from urban centers. WSOC and CO were highly correlated ($r^2 > 0.78$) in these urban plumes. The ratio of the enhancement in WSOC relative to CO enhancement was found to be low ($\sim 3 \mu\text{g C/m}^3/\text{ppmv}$) in plumes that had been in transit for a short time, and increased with plume age, but appeared to level off at $\sim 32 \pm 4 \mu\text{g C/m}^3/\text{ppmv}$ after ~ 1 day of transport from the sources. The results suggest that the production of WSOC in fine particles depends on compounds coemitted with CO and that this process is rapid with a time constant of ~ 1 day.

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1. Introduction

[2] The carbonaceous component remains one of the least understood chemical fractions of ambient particles. These compounds are important because they can comprise a large fraction of the PM_{2.5} mass, 10 to 70% [Andrews *et al.*, 2000; Quinn and Bates, 2003], and may influence atmospherically important properties of aerosol particles. Organic carbon (OC) is directly emitted from a wide range of sources including combustion of fossil fuels, biomass burning, direct injection of unburnt fuel and lubricants, plant matter, industrial emissions, and biogenic emissions [Jacobson *et al.*, 2000]. Studies suggest that under many conditions a large fraction of the ambient OC can be produced from

secondary organic aerosol (SOA) formation from combustion sources and biogenic emissions. The myriad of carbonaceous sources leads to organic aerosol particles composed of a vast number of compounds ranging from highly water-soluble to insoluble. Because of its chemical complexity, only a small fraction of these compounds has been identified [Schauer *et al.*, 1996; Hamilton *et al.*, 2004].

[3] One approach to study the organic fraction is to chemically group organic compounds by properties of atmospheric relevance. The organic fraction that is soluble or partially soluble in water is one example of such a chemical grouping. Water-soluble organic carbon (WSOC) in aerosol particles is not well studied in part because most previous organic carbon analyses has involved GC (gas chromatography) separation methods that are not readily amendable to polar compounds (many water-soluble organic compounds are thought to be highly polar). WSOC is of interest because it is often the majority of the carbonaceous component, ranging from ~ 30 to 80% , depending on location and season [Zappoli *et al.*, 1999; Decesari *et al.*, 2001; Jaffrezo *et al.*, 2005].

[4] Water is a ubiquitous atmospheric component and the chemical nature of the particle determines the amount of

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condensed water that is associated with particles. Past work has focused on the role of inorganic ions on particle water uptake; however, the organic fraction also influences these processes. For example, in liquid clouds, water-soluble organic compounds may contribute to or impede the ability of aerosol particles to act as cloud condensation nuclei (CCN) [Novakov and Penner, 1993; Novakov and Corrigan, 1996; Facchini *et al.*, 1999]. These compounds may also affect particle hygroscopicity, or the uptake of water vapor under subsaturated conditions. Saxena *et al.* [1995] provide evidence that particle-phase organics enhance water uptake by atmospheric particles in some locations and retard water uptake in other locations. In a nonurban area (the Grand Canyon) the presence of organic compounds enhanced the water absorption by particles and accounted for 25 to 40% of the total water uptake. In an urban area (Los Angeles) the presence of organic compounds inhibited water uptake by about 25 to 35%. These interactions between particle chemistry and water vapor can affect visibility and the global radiation budget. The hygroscopic nature of individual particles can also influence their atmospheric lifetimes, which are often dictated by precipitation scavenging.

[5] There are many known sources for organic compounds that are soluble in water. These include both primary emissions and secondary products from biogenic and anthropogenic sources. Motor vehicle emissions may directly produce aliphatic and aromatic acids and aldehydes. Aliphatic acids and aldehydes can also be directly emitted from biogenic sources. In addition, gaseous aliphatic and aromatic anthropogenic volatile organic compounds (VOCs) can produce particulate aliphatic and aromatic carboxylic acids and aldehydes via SOA formation [Kawamura *et al.*, 1985; Khwaja, 1995; Forstner *et al.*, 1997; Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts, 2000]. Biogenic emissions of VOCs, such as pinene, can produce cyclic acids and long-chain aldehydes as SOA products [Seinfeld and Pandis, 1998; Glasius *et al.*, 2000]. Biogenic isoprene may also lead to SOA [Pandis *et al.*, 1991; Edney *et al.*, 2005], especially under high-NO_x conditions [Kroll *et al.*, 2005]. Organic carbon in aerosol particles produced from biomass burning has been shown to be predominately aliphatic, composed mainly of oxygenated compounds with a minor content of aromatic compounds containing carboxylic acids and phenols [Graham *et al.*, 2002]. Measurements also suggest biomass burning aerosol contains a significant amount of poly acidic compounds (e.g., HULIS) [Mayol-Bracero *et al.*, 2002b]. Many of the biomass burning compounds are water-soluble [Novakov and Corrigan, 1996; Narukawa *et al.*, 1999; Graham *et al.*, 2002; Mayol-Bracero *et al.*, 2002b].

[6] The measurement of these WSOC compounds is somewhat operationally defined since the WSOC concentration may depend on how the ambient particles were collected and isolated. For example, WSOC extracted from filters may depend on the mechanical method used to remove soluble compounds from the filter, the use of liquid filtration, and the degree of dilution and resulting liquid concentration. (Results from comparisons between online and off-line WSOC measurements are discussed below.) In the latter issue, different solubilities of specific organic

constituents of WSOC may influence measured WSOC concentrations.

[7] The most widely used WSOC sampling technique involves collection of aerosol particles on prebaked quartz fiber filters followed by manual extraction and analysis. There are, however, drawbacks associated with this method. To obtain sufficient mass for analysis of organic carbon, sampling times on the order of hours or greater are typical. These long sampling times limit investigations into the WSOC sources and the processes that affect ambient concentrations. Extended sampling periods can also lead to artifacts. Positive artifacts occur when gas phase carbonaceous material is captured and analyzed with the particulate matter. Loss of semivolatile organic material collected on a filter during sampling will lead to negative artifacts (under measurement). This is exacerbated during long sampling periods that tend to expose collected particles to wider ranges in ambient conditions during the sampling period (e.g., temperature, relative humidity) [McDow and Huntzicker, 1990].

[8] To date, most measurements of carbonaceous aerosol have been made at surface sites; however, quantitative airborne measurements of the carbonaceous fraction can be of significant value since they provide information on spatial distributions and facilitate the study of aerosol plume chemical evolution. Measurements of aerosol organic carbon have been made from aircraft over the east coast of the United States [Novakov *et al.*, 1997], the Indian Ocean [Mayol-Bracero *et al.*, 2002a], over southern Africa during the dry biomass burning season [Kirchstetter *et al.*, 2003], and over the western Pacific Ocean in outflow from the Asian continent [Huebert *et al.*, 2004]. In all cases particles were collected onto prebaked quartz filters. Huebert *et al.* [2004] used an off-line thermal/optical analyzer for the carbon analysis (Sunset Labs, Forest Grove, Oregon), whereas the other three studies used evolved gas analysis. Maria *et al.* [2002, 2003] have made airborne measurements of organic carbon functional groups with Fourier transform infrared (FTIR) analysis of solvent extracted filters. Kawamura *et al.* [2003] measured specific water-soluble dicarboxylic acids over East Asia and the western North Pacific using GC/MS (gas chromatograph/mass spectroscopy) analysis of quartz filter extracts. When deployed on aircraft these methods are limited by long sampling times leading to few data points and poor spatial resolution. Detection limits were typically poor and artifacts an issue.

[9] Measurements based on mass spectrometers have recently been used to quantify carbonaceous aerosol online from aircraft [Bahreini *et al.*, 2003]. These methods provide unique size-resolved data of the volatile fraction of the aerosol particles, and chemically group the carbonaceous material by their mass spectra. Bahreini *et al.* [2003] reported a detection limit of 11.7 $\mu\text{g}/\text{m}^3$ for 1 min averages, although newer instruments have significantly lower detection limits.

[10] This paper reports on a quantitative method for rapid 3 s online measurement of the bulk WSOC component of aerosol particles. The approach is an extension of our method used for online measurements of water-soluble inorganic compounds involving a particle-into-liquid sampler (PILS) coupled directly to ion chromatographs (IC) [Weber *et al.*, 2001; Orsini *et al.*, 2003]. A detailed descrip-

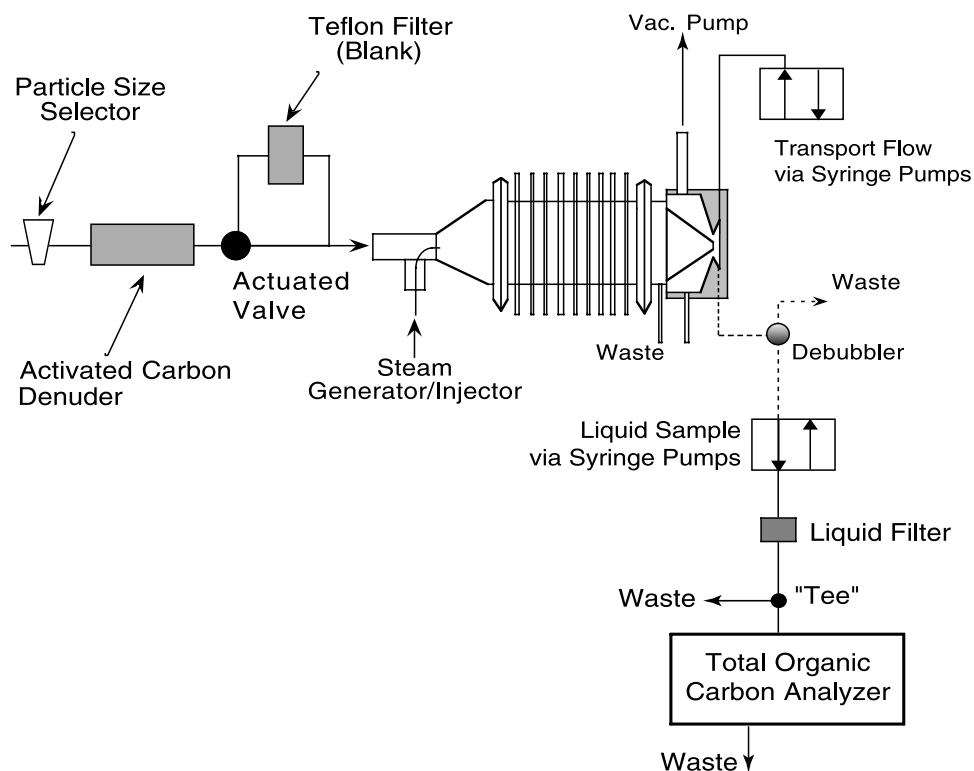


Figure 1. Schematic of the particle-into-liquid sampler coupled to a total organic carbon (TOC) analyzer for measurement of bulk fine particle (PM_{10} or $PM_{2.5}$) organic constituents soluble in water.

tion of the method and results from airborne measurements of the WSOC during the National Oceanic and Atmospheric Administration (NOAA) sponsored New England Air Quality Study/Intercontinental Transport and Chemical Transformation (NEAQS/ITCT) 2004 mission conducted in the northeastern United States are presented.

2. Methods

2.1. Particle Collection Method

[11] The method for capturing ambient particles into purified water with the particle-into-liquid sampler (PILS) for online analysis is described only briefly since details have been published [Orsini *et al.*, 2003]. Ambient particles are directed into a liquid stream by growing the particles under supersaturated conditions through rapid mixing of saturated water vapor with ambient aerosol. Activated particles grow to sizes from 1 to 5 μm in diameter and are then collected by an inertial impactor. An accurately metered and adjustable flow of deionized water (DI Water) is pumped across the impaction plate and mixes with the sample drops collected on the impaction plate to produce a continuous liquid sample that can be analyzed and quantified by an online technique.

[12] To adapt the PILS for a WSOC measurement, minor modifications were made to the PILS-IC method. These changes included an activated carbon parallel plate denuder [Eatough *et al.*, 1993] to remove organic gases, a method for online and frequent background measurements, syringe pumps for delivery of the liquid sample,

and an in-line liquid filter. A schematic of the system is shown in Figure 1.

2.2. Minimization of Background Interferences and Limits of Detection

[13] Efforts were made to minimize positive interferences from background carbonaceous material in the sampling system to permit quantitative measurements and improve detection limits. Background organic carbon in the PILS-TOC system comes from the organic carbon found in DI Water, organic carbon that can desorb from the walls of the liquid sample lines, and any organic gases not removed by the denuder and absorbed in the liquid drops and liquid collection system. To determine the concentration of only particulate organic carbon, the real background was determined using a dynamic blank, similar to the approach used in other online carbonaceous measurements [Lim *et al.*, 2003]. A normally opened actuated valve was periodically closed via an external timer, or computer with appropriate interface, forcing the sample airflow through a Teflon filter (see Figure 1). Other studies have suggested that Teflon is an appropriate choice since it efficiently removes particles but not interfering gases [McDow and Huntzicker, 1990; Turpin *et al.*, 1994]. For ground-based studies, a background measurement was made every 4 hours for a half hour, whereas for airborne operation a background measurement was made every 2 hours for 10 min. In both ground and aircraft measurements, the instruments were completely automated. As with ground measurements, in these airborne measurements there was a substantial background signal that was different from the measured signal.

There was no evidence that this background signal depended upon aircraft altitude and the background values within a single flight were fairly constant. For example, for the flight on 27 July 2004 the average background was 11.6 ppb C with a variability, based on one standard deviation, of 2.8 ppb C. For comparison, the average nonfiltered WSOC liquid concentration for this flight was 23 ppb C. The background also did not depend strongly on ambient concentration. A background measurement conducted in an urban plume where ambient WSOC concentrations were high (~ 55 ppb C) was only slightly higher than background measurements (~ 15 ppb C) made under clean conditions (i.e., ~ 5 ppb C higher than average of other background measurements within that flight). These results are consistent with earlier findings [Sullivan *et al.*, 2004] that most background signal was from contaminants in the purified water employed in the PILS system. The greatest variation in the background signal from flight to flight was due to differences in supply water purity. A reduction in the background would improve detection limits. This may be possible by oxidizing background organic carbon to carbon dioxide just prior to delivering sample water to the PILS.

[14] The standard deviation in the background concentrations was approximately $0.3 \mu\text{g C/m}^3$. However, as evidenced through comparisons with other measurements such as particle volume, the precision of the WSOC signal over short periods of flight is sufficient to allow use of the data at concentrations as low as $0.1 \mu\text{g C/m}^3$. Absolute concentrations between 0.1 and $1 \mu\text{g C/m}^3$ are more uncertain however. Absolute uncertainties are discussed in more detail below. Ambient WSOC was calculated as the difference between ambient and background (filtered air) measurements, where background concentrations were assumed constant between consecutive background measurements. All reported WSOC concentrations are at conditions of 1 atmosphere and 293 K.

2.3. Liquid Handling System

[15] The liquid sample extracted from the PILS was filtered in-line prior to the TOC measurement to remove any insoluble particles. Both $0.5 \mu\text{m}$ PEEK (polyether-etherketone) and $0.22 \mu\text{m}$ polypropylene filters were tested; no significant difference in instrument response was observed between the two filter types. During continuous ground-based measurements at an urban site a $0.5 \mu\text{m}$ filter required daily changes to limit pressure drops across the filter. During this airborne experiment the $0.5 \mu\text{m}$ filter was changed every second or third flight, despite apparently little increase in filter pressure drop.

[16] Employing a liquid filter requires that the liquid sample be pressurized to force it through the filter. A continuous flow of liquid sample was pushed through the liquid filter and delivered to the TOC analyzer using two syringe pumps (Versa 3, Kloehe Inc., Las Vegas, Nevada) in “handshaking” mode with 2.5 mL syringes. In addition, two similar pumps were used to supply the transport DI Water to the top of the PILS impaction plate. Use of glass syringe pumps versus a peristaltic pump with polymer

tubing reduces background WSOC. All liquid sample lines were narrow bore (0.5 mm ID) PEEK tubing.

2.4. TOC Analyzer and Coupling to PILS

[17] A Sievers Model 800 Turbo TOC analyzer (Boulder, Colorado) quantified the WSOC content of the liquid sample by converting all organic carbonaceous material to carbon dioxide using chemical oxidation involving ammonium persulfate and UV light. Carbon dioxide formed is then directed through a semipermeable membrane into a flow of DI Water whose conductivity is measured. The increase in conductivity of the DI Water is proportional to the concentration of aqueous carbon dioxide in the DI Water stream, which is proportional to the concentration of aqueous carbon dioxide formed from the sample. The difference between a total carbon channel and inorganic carbon channel is used to determine the organic carbon concentration. Carbonaceous material in the total carbon channel is oxidized, whereas the inorganic carbon channel is unaltered. The TOC analyzer runs off of an internal calibration performed in the factory. This calibration was periodically verified with an oxalic acid standard and was typically within 5% of the factory calibration. More information about this analyzer and its calibration is given by Sullivan and Weber [2006a].

[18] A continuous liquid sample flow was drawn by an internal peristaltic pump into the TOC analyzer for analysis. Since syringe pumps are used to draw the liquid sample from the PILS and force it through a filter for delivery to the TOC, and exact flow matching is not possible, the liquid sample line after the filter cannot be directly coupled to the TOC. As shown in Figure 1, a “tee” was added downstream of the liquid filter prior to the TOC analyzer with one leg going to waste. For airborne deployment this means the liquid sample was near cabin pressure prior to entering the TOC analyzer, which enabled the TOC analyzer to operate in its normal mode and to control the sample flow by its internal pump. The transport flow was adjusted so that the waste leg flow rate was minor (less than 0.1 ml/min) but always positive. The debubbler and “tee” were constructed of Pyrex with an internal volume less than 0.05 ml .

2.5. Artifacts and Measurement Uncertainty

[19] Gas denuding and background correction are used to minimize positive artifacts due to absorption of gases. To limit reequilibration between the condensed and vapor phases during the interval between gas denuding and activation within the PILS, at which point the particles become very dilute drops, the denuder was situated as close to the PILS entrance as possible ($\sim 0.15 \text{ s}$ residence time).

[20] Negative artifacts associated with evaporation of semivolatile organics can also lead to a biased measurement. Evaporation of semivolatile organic material may happen because of ram heating at the aircraft aerosol inlet or because of heat transfer in the sample lines between the inlet and the instrument. Measurements of sample temperature at the PILS inlet indicate that sample air was typically 12 K higher than ambient for measurements at altitudes up to 2 km, and 30 K for measurements between 3 and 4 km. (These are the altitudes where WSOC concentrations are investigated in most detail.) Additionally, elevated temperatures in the droplet-forming region and sample collection

Table 1. Summary of the Differences in the Liquid Flow Rates and Analyzer Mode for Ground-Based and Airborne PILS-TOC Measurements

	Ground-Based	Airborne
Flow rate of transport water over impactor, ml/min	0.6	1.4
Flow rate of sample liquid out of the impactor and through the liquid filter, ml/min	0.5	1.3
TOC analyzer liquid sample flow rate, ml/min	0.4	1.2
TOC analyzer sample mode and integrated sample time	online, 6 min	turbo, 3 s
Duration of background measurement	30 min	10 min

surfaces in the PILS could lead to further losses of semi-volatile organic species. Lacking knowledge of the specific composition and vapor pressures of the WSOC in the aerosol, we have not attempted to account for these biases. However, closure of the particle mass budget relative to measured particle volume (C. A. Brock et al., manuscript in preparation, 2006) and the aerosol mass spectrometer (AMS) composition observations suggest that any systematic bias due to particle volatility is not of consequence to the findings presented here.

[21] The uncertainty associated with the WSOC measurement can be estimated by combining the uncertainties in various flow rates, the method for determining the liquid carbonaceous concentration, and uncertainties in the background variability. Liquid concentrations cannot be measured as precisely in the PILS-TOC system as the PILS-IC system where dilution due to added liquid from collected drops and wall condensate to the impactor plate can be determined by spiking the transport flow with lithium (or other appropriate ions not in the ambient aerosol). Recording the change in lithium measured upstream and downstream of the impactor provided a measure of dilution in the PILS-IC system. A similar approach cannot be used in the PILS-TOC for measurement of WSOC. On the basis of experiments with a PILS-IC operated identically to the WSOC system, a constant dilution factor of 1.17 is assumed. The relative uncertainty in assuming a constant value is estimated to be $\pm 4\%$.

[22] Variability in backgrounds can lead to uncertainty since a background measurement is made only periodically, whereas we assume that the background is constant between consecutive background measurements. On the basis of the measured background variability this component of the uncertainty is estimated to be typically $\pm 0.3 \mu\text{g C/m}^3$. Combining the known uncertainties (5% flows, 4% dilution, and 5% TOC calibration) the overall measurement uncertainty is estimated to be approximately $\pm 8\% + 0.3 \mu\text{g C/m}^3$. Most biases are expected to be negative, such that the WSOC reported here is a lower limit.

2.6. Airborne WSOC Measurement Methods: Modified Flow Rates to Improve Response Times

[23] The system described can be deployed for either ground-based or airborne measurements. However, for aircraft measurements a rapid sampling rate and fast response time is desired. Thus, for airborne measurements the TOC was operated in Turbo mode, providing a measurement every 3 s, and liquid flow rates were increased to improve system response. Table 1 summarizes the differences in operating parameters for ground and airborne measurements.

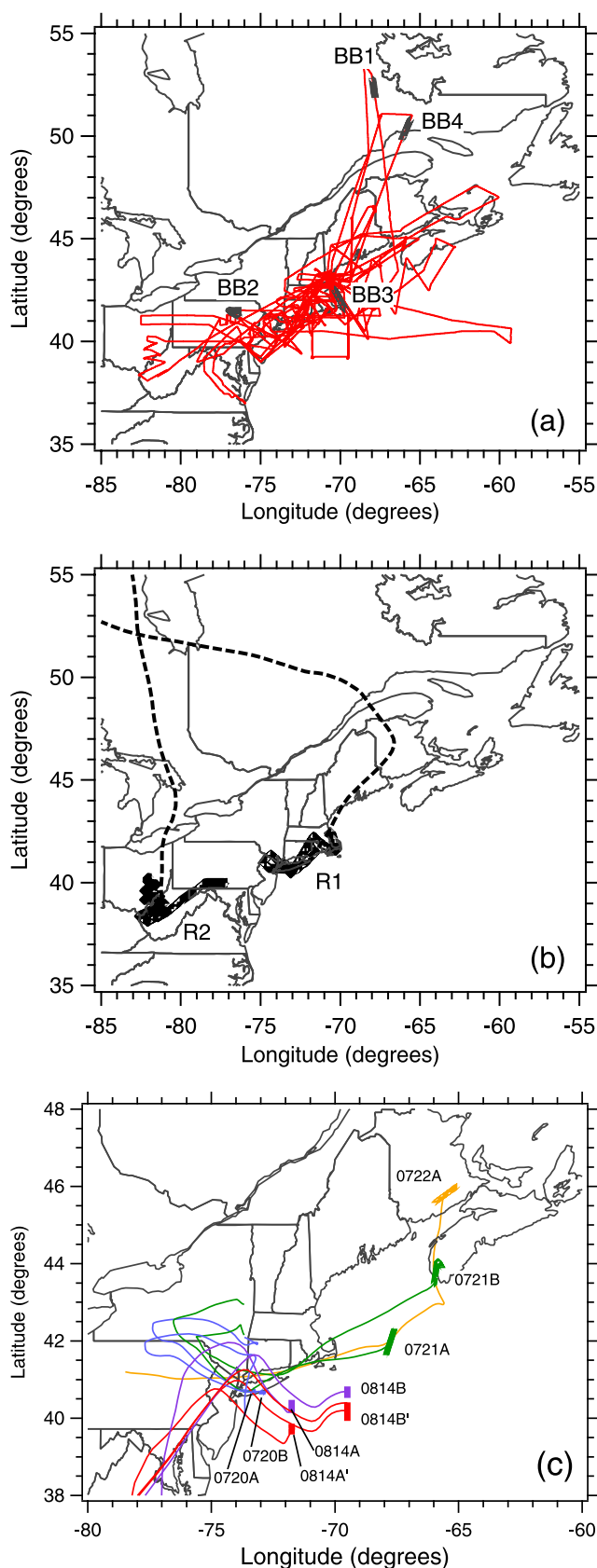
[24] Liquid-based systems may respond slowly to rapidly changing concentrations due to mixing in the various components that transmit the collected sample to the detector, and within the detector itself [Sorooshian et al., 2006]. Improved response times can be achieved in the liquid transport components by minimizing volumes, for example by using narrow bore tubing, and small volume debubblers, liquid filters, and syringe pumps. Within the TOC detector itself, higher flow rates are the only feasible way to improving response times. By injecting an oxalic acid standard into the TOC analyzer, experiments on TOC response time were performed to determine optimal liquid sample flow rates. The resulting change in measured concentration was recorded and the time for a concentration change from 10% to 90% of the step increase determined. It was found that the TOC analyzer response time was approximately inversely proportional to the sample flow rate. Doubling the specified Turbo mode flow rate of the TOC analyzer from 0.6 to 1.2 ml/min improved the response time of our analyzer to approximately 1 min. The higher liquid flow rate improves the responsiveness of the complete system, however, this also results in a more dilute sample.

[25] To assess the response time of the complete system, comparisons were made between a 1 s measurement of CO and the 3 s WSOC recorded during this aircraft mission. On the basis of an analysis of two plumes with sharp edge transitions (the plumes analyzed are shown in Figures 4 and 6b) the response time is estimated to be between 45 to 65 s. Slow response is believed to be mainly from mixing in the syringe pumps. Employing smaller volume syringes should improve the response.

[26] The time for particles collected in the liquid within the PILS to be detected by the TOC, referred to as the delay time, was determined by measuring the transit time of an air bubble from the PILS impactor, through the entire liquid system, to the entrance of the TOC analyzer. The data were corrected for this 288 s time lag in the measurement. Overall, the effect of response and delay times tends to make the WSOC measurement most imprecise during periods of sharp changes in concentration.

2.7. Comparison Between Online and Integrated Filter Measurements of WSOC

[27] Online measurements of WSOC with the PILS coupled to a TOC analyzer have been compared to off-line measurements of WSOC. The PILS-TOC was run in a manner similar to that discussed above. The off-line measurement involved manual extraction of typically 24 hour integrated filters and subsequent analysis similar to the online method, including liquid filtration and TOC detec-



tion. Comparisons were made during studies conducted at two urban sites; Atlanta, GA and Tokyo, Japan. In both studies nondenuded integrated filter measurements were approximately 10% higher than the denuded online WSOC, and the two methods were highly correlated (linear regression r^2 in Atlanta and Tokyo were 0.83 and 0.89, respectively) [Miyazaki *et al.*, 2006; Sullivan and Weber, 2006b].

2.8. Airborne Mission and Other Measurement Methods

[28] The NOAA sponsored NEAQS/ITCT 2004 airborne mission was part of the larger International Consortium for Atmospheric Research on Transport and Transformation (ICARTT). The NOAA WP-3D was operated out of Portsmouth, New Hampshire, from 9 July to 15 August 2004. As part of this multi-investigator field study, measurements were made of a suite of aerosol particle physical and chemical properties, and of several reactive and trace gases. The aerosol measurements included bulk concentrations of the ionic constituents and WSOC of particles with aerodynamic diameters $<1.0 \mu\text{m}$ (PM_{10}) using the PILS-IC and TOC systems, respectively. Several flights focused on investigating sources, transport, mixing, and chemical transformations of anthropogenic emissions from the urban corridor along the east coast, which likely included emissions from Boston, New York, Philadelphia, and Baltimore. A map of the flight paths is shown in Figure 2a.

[29] The PILS-TOC sampled from a Low Turbulence Inlet (LTI) [Wilson *et al.*, 2004], as did the PILS-IC system, the AMS, and a coarse mode optical particle counter. With a combined flow of 30.5 L/min, these three instruments shared a sample line that included a nonrotating MOUDI impactor [Marple *et al.*, 1991] with 50% transmission efficiency at $1.0 \mu\text{m}$ at 1 atmosphere ambient pressure. The flow was then split to individual instruments.

[30] In the following analysis we focus on the sources of submicron WSOC during this experiment. Additional measurements used in the analysis include gaseous organic compounds measured by a proton transfer reaction-mass spectrometer (PTR-MS) approximately every 18 s [de Gouw *et al.*, 2003a] and 1 s carbon monoxide (CO) [Holloway *et al.*, 2000]. Inorganic aerosol chemical components were measured with a PILS coupled to a cation and anion ion chromatograph with a sampling rate of 2.45 min. PM_{10} volume with 1 s resolution was determined from number size distributions constructed from the measurements of three instruments [Brock *et al.*, 2000, 2004]. A condensation particle counter (CPC) measured concentrations in five particle size ranges from $0.004 \mu\text{m}$ to $0.055 \mu\text{m}$ diameter. A modified LasAir 1001A laser optical particle counter (OPC) measured concentrations in 64 size bins from $0.15 \mu\text{m}$ to $0.95 \mu\text{m}$ diameter. A white light optical particle

Figure 2. (a) Map of aircraft flight paths during NEAQS/ITCT 2004. In Figure 2a, measurement locations of various biomass burning plumes (BB1 through BB4) are identified. (b) Back trajectory for rural plumes (R1, R2). (c) Characteristic air mass back trajectories for each of the nine urban plumes discussed in the analysis. All back trajectories are based on the NOAA ARL HYSPLIT trajectory model.

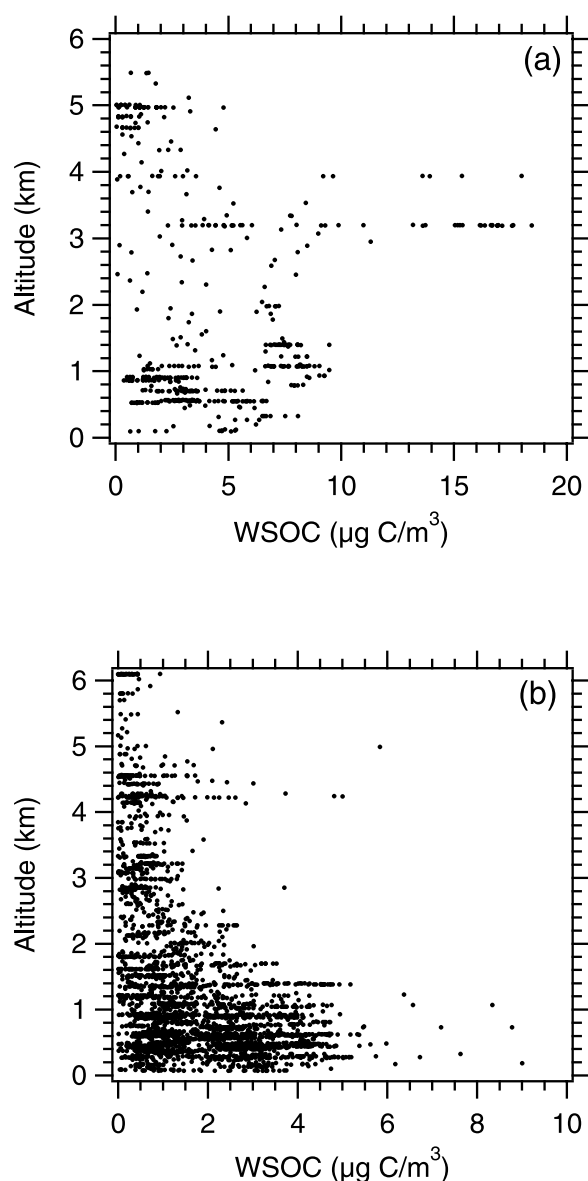


Figure 3. One-minute averaged PM_{10} WSOC concentrations as a function of altitude for all data collected during the experiment. Data are separated into (a) biomass burning (acetonitrile > 250 pptv) and (b) non-biomass burning (acetonitrile < 250 pptv) WSOC.

counter (WLOPC) was located inside the aircraft and measured size bins from $0.7\ \mu\text{m}$ to $8.0\ \mu\text{m}$ diameter. An instability observed with the WLOPC that resulted in an upward shift in the measured size distribution was corrected so that the overlapping distributions ($0.7\text{--}0.95\ \mu\text{m}$ diameter) of the OPC and WLOPC agreed. Sampled air was heated to 35°C for the CPC, but was not heated in the case of the OPC. The volume was measured at a relative humidity (RH) less than ambient, up to 40% RH. If higher than 40% RH, the volume was adjusted to 40% RH on the basis of the hygroscopic diameter growth for mixed sulfate/organic particles as described by Santarpia *et al.* [2004]. Thus the influence of water on particle mass is expected to be minor since at 40% RH water accounts for only about 6% of the mass [Santarpia *et al.*, 2004]. Consistent with the

WSOC measurements, concentrations are reported at 293K and 1 atmosphere.

3. Results of Airborne Measurements of WSOC During NEAQS/ITCT 2004

[31] During this study, substantially enhanced WSOC concentrations were associated with biomass burning plumes and plumes emanating from urban centers. Figures 3a and 3b show the measured WSOC concentration as a function of altitude, delineated into biomass and non-biomass influenced air masses. Acetonitrile was used as a unique biomass burning tracer [de Gouw *et al.*, 2003b]. In this paper we identify air masses with a biomass burning influence by acetonitrile concentrations above 250 pptv, assuming 250 pptv and below are background acetonitrile concentrations. It cannot be completely excluded that some biomass burning influence may persist in the data with below 250 pptv acetonitrile, but it is likely to play a very minor role. Most concentrated biomass plumes were detected in layers generally between altitudes of 3 and 4 km, however, evidence of a biomass influence (based on acetonitrile above 250 pptv) was observed over all measured altitudes. For non-biomass burning data, WSOC concentrations were highest near the surface and decreased with altitude, similar to sulfate, the other major aerosol chemical constituent.

3.1. Biomass Burning WSOC

[32] A variety of studies report that significant fractions of biomass burning smoke particles have carbonaceous components that are soluble in water [Novakov and Corrigan, 1996; Narukawa *et al.*, 1999; Graham *et al.*, 2002; Mayol-Bracero *et al.*, 2002b]. A similar result was observed in this experiment; measured WSOC was highly correlated with fine particle volume and known gaseous biomass burning emissions, such as acetonitrile and carbon monoxide. More detailed discussions on biomass burning plumes measured during this mission are given by de Gouw *et al.* [2006] and A. G. Wollny *et al.* (manuscript in preparation, 2006).

[33] The locations of four large and distinct biomass plumes are given in Table 2 and identified on the map in Figure 2a. These plumes were all intercepted within layers between 3 and 4 km altitude (see Figure 3a). A Lagrangian air particle dispersion model (FLEXPART [Stohl *et al.*, 2002]) indicated that these plumes were from biomass burning in the Alaska/northwestern Canada region and transported to the point of measurement over periods ranging from 4 to 10 days [de Gouw *et al.*, 2006]. In all cases the WSOC was highly correlated with acetonitrile and CO, with r^2 ranging between 0.88 and 0.96 (see Table 2). An exception was the biomass plume intercepted on 21 July 2004 (BB3) in the vicinity of Boston with a lower WSOC-CO r^2 of 0.71. Overall, these biomass plumes contained the highest concentrations of WSOC and PM_{10} volume observed throughout the entire airborne experiment.

[34] As an example of a specific biomass plume interception, Figure 4 shows the time series of the WSOC, fine particle volume, CO, and acetonitrile for the biomass plume intercepted on 9 July 2004 (BB1, Table 2 and Figure 2a). It can be seen that all four of these measurements are highly correlated within the plume.

Table 2. Characteristics of Four Major Biomass Burning Plumes Intercepted by the WP-3D^a

	9 Jul 2004, 2006–2020 UTC (BB1) ^b	20 Jul 2004, 1722–1737 UTC (BB2)	21 Jul 2004, 1951–2003 UTC (BB3)	28 Jul 2004, 1642–1656 UTC (BB4)
WSOC, $\mu\text{g C/m}^3$	8.13 (0.57, 18.00) [7.76]	14.54 (5.83, 18.45) [11.36]	12.56 (5.54, 16.70) [11.58]	13.24 (6.04, 17.63) [10.42]
CO, ppbv	362 (110, 633) (11)	325 (216, 410) (164)	278 (136, 419) (111)	299 (177, 363) (197)
Acetonitrile, pptv	844 (279, 1491) (469)	775 (278, 904) (463)	709 (292, 947) (447)	555 (372, 627) (344)
PM ₁ volume, $\mu\text{m}^3/\text{cm}^3$	80.6 (3.47, 181) [74.4]	70.3 (9.58, 91.8) [63.0]	65.1 (19.5, 103) [59.6]	78.1 (14.1, 104) [68.0]
Transport time, ^c days	6–8	8–10	8–10	4–5
Latitude, deg	52.32	41.42	41.98	50.32
Longitude, deg	–67.90	–76.71	–69.99	–65.87
Altitude, m	3936	3161	3200	3197
WSOC-acetonitrile r^2	0.95	0.92	0.93	0.89
WSOC-CO r^2	0.96	0.92	0.71	0.89
$\Delta\text{WSOC}/\Delta\text{CO}$, ^d $\mu\text{g C/m}^3/\text{ppmv}$	39.4	69.4	125.6	78.7
WSOC/PM ₁ volume, $(\mu\text{g C/m}^3)/(\mu\text{m}^3/\text{cm}^3)$	0.10	0.22	0.19	0.17

^aIncluded are the mean, in parenthesis the maximum and minimum values, and in brackets the average concentration increase within the plume relative to local background (all based on 1 min averaged data). Local time is EDT = UTC – 4 hours.

^bBB1, BB2, BB3, and BB4 are used to identify the specific biomass plumes in Figure 2a.

^cCalculated on the basis of the FLEXPART model.

^dThis ratio is the change in WSOC relative to CO within the plume above the local background concentrations for each case. Background concentrations were determined from measurements at roughly the same altitude near each plume.

[35] Other less distinct biomass burning plumes were also present throughout the study. Some were observed at lower altitudes and mixed with local anthropogenic sources. Back trajectory analysis suggests all of these air masses were from the Alaska/northwestern Canada fires. Although the aircraft did not measure down to the surface, other analysis show that these emissions influenced ground-level local air quality during the period of the measurement campaign (R. B. Pierce and J. Szykman, personal communication, 2003).

3.2. Non-Biomass Burning WSOC

[36] Although biomass plumes occasionally led to greatly enhanced WSOC concentrations throughout the study domain, other known major sources of WSOC are secondary and possibly primary organic compounds from biogenic emissions and mobile sources. To investigate these other non-biomass burning sources of WSOC, the biomass burning events were removed by considering only data for which acetonitrile was below 250 pptv (see Figure 3b).

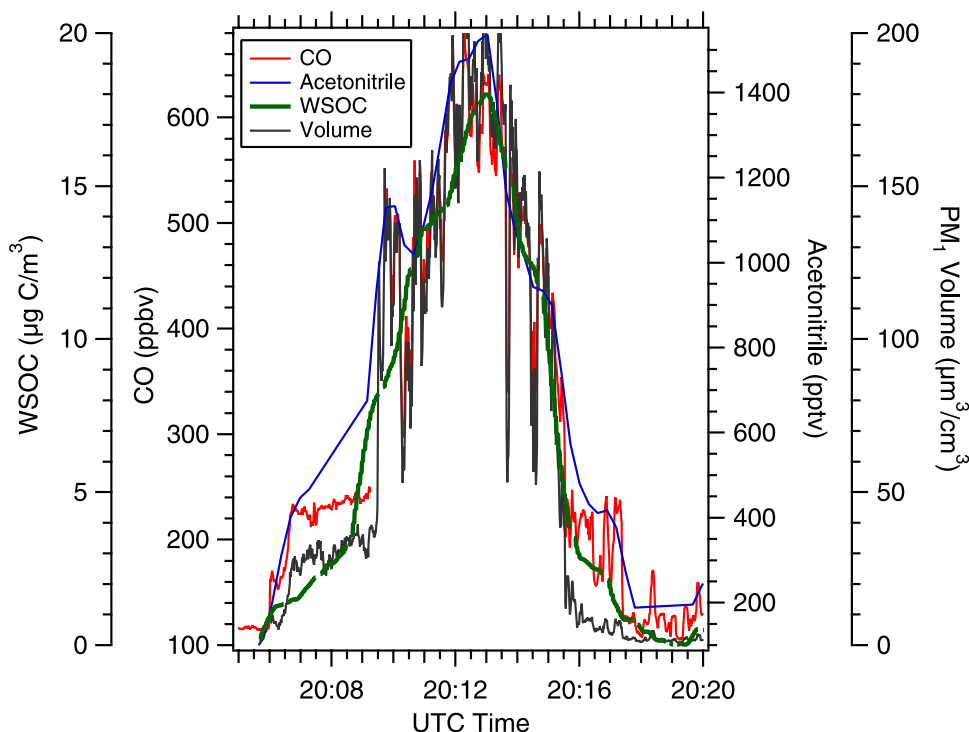


Figure 4. Time series of 3 s WSOC, fine particle volume, carbon monoxide, and acetonitrile recorded in the biomass plume BB1 (identified in Figure 2) on 9 July 2004. Local time is EDT = UTC – 4 hours.

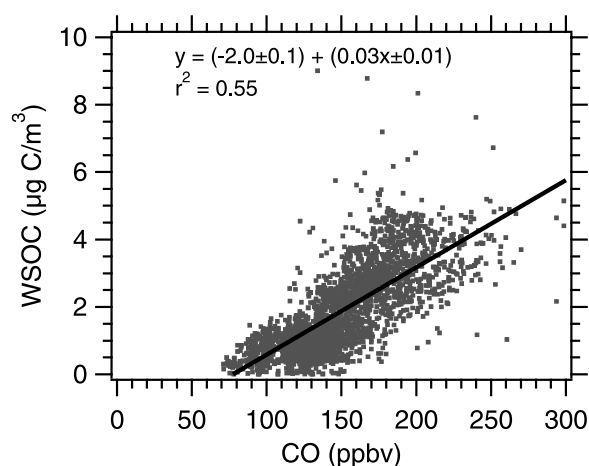


Figure 5. Correlation between 1 min averaged WSOC and CO for all non-biomass burning influenced measurements (acetonitrile < 250 pptv) recorded below 2 km altitude during the experiment. Uncertainties associated with the least squares regression are one standard deviation.

Apart from biomass burning emissions, SOA from biogenic and anthropogenic precursors will both lead to WSOC. Emission inventories for biogenic compounds, such as isoprene and terpenes, suggest that significant sources exist in the northeastern states, especially the northern part of Maine, and northern regions of Ontario and Quebec (<http://map.ngdc.noaa.gov/website/al/emissions/viewer.htm>). Air masses from these regions were sampled during this experiment. In the following analysis only measurements made below 2 km altitude are analyzed to investigate these non-biomass burning surface sources for WSOC.

3.2.1. WSOC-CO Correlation

[37] As in the biomass burning plumes, WSOC was also found to be correlated with CO in urban plumes without a biomass burning influence. For all data measured when altitude was below 2 km and acetonitrile less than 250 pptv, WSOC and CO are positively correlated ($r^2 = 0.55$, see Figure 5). A number of individual plumes from urban centers, such as New York City, Boston, and Philadelphia, were intercepted at various times during the experiment. The measurement locations for 9 different plumes are shown in Figure 2c and the WSOC and CO concentration time series for three selected plumes are shown in Figure 6. WSOC and CO were well correlated in the urban plumes ($r^2 > 0.78$) and have higher correlations than the combined mission data set (see Table 4 for a summary). Since CO in urban centers is mainly from vehicle emissions [U.S. Environmental Protection Agency, 1997], these data suggest that mobile sources are linked to the observed WSOC.

3.2.2. Urban Versus Background Rural

[38] In order to compare the urban WSOC concentrations to more rural background air masses, and to search for possible evidence of a biogenic source for WSOC, the FLEXPART Lagrangian air particle dispersion model [Stohl *et al.*, 2002] was used to identify air masses lacking significant influences from urban CO sources. As an example, concentrations measured in two air masses are shown in Table 3. The air masses were sampled during two flights, 25 July 2004 and 6 August 2004. The locations where they

were encountered and representative air mass back trajectories are shown in Figure 2b. These air masses had passed over Canada and the Great Lakes, or Canada and New England, at altitudes between 800 to 1800 m within 2 days of the measurement.

[39] Emission inventories for the regions where these air masses had recently advected over show significant biogenic VOC sources. Estimated relative emission levels are between ~ 50 –173 (moles of isoprene)/(km² hr) or ~ 0.68 –11.50 (moles of terpenes)/(km² hr) (<http://www.epa.gov/asmdnerl/biogen.html>). It is likely that the air masses contain aerosol particles that are representative of the background aerosol found in the northeastern United States and Canada, with potentially a significant biogenic influence. These rural air masses were found to have some of the lowest low altitude (<2 km) CO and WSOC concentrations of the mission (see Table 3). The CO ranged from 99 to 177 ppbv. The 25 percentile for CO was 117 ppbv. For WSOC, the range was from 0.43 to 2.13 $\mu\text{g C/m}^3$, with the WSOC 25 percentile at 0.72 $\mu\text{g C/m}^3$.

3.2.3. WSOC Evolution in an Urban Plume

[40] Urban centers are a major source of WSOC measured in this study with concentrations factors of 2 to 3 times higher than background air masses (compare Tables 3 and 4). The range of WSOC concentrations observed for the urban influenced air during this study is comparable to WSOC recorded on the ground in urban Atlanta and St. Louis, where typical summer concentrations range from 2 to 4 $\mu\text{g C/m}^3$ [Sullivan *et al.*, 2004; Sullivan and Weber, 2006a].

[41] Secondary organic aerosol formation is expected to produce WSOC, and thus WSOC to CO ratios may be expected to increase with plume age. To investigate relative changes in CO and WSOC within these urban plumes, an estimate of the background concentrations of CO and WSOC is required. Analysis of rural air masses advecting toward the urban regions suggest background concentrations of the order of 125 ppbv for CO and 1 $\mu\text{g C/m}^3$ for WSOC. Background concentrations can also be estimated from measurements made near the various plumes. For example, in Figure 6 regions of low CO likely representative of local background conditions are recorded near the identified urban plumes. Background conditions near the urban plumes were near 141 ppbv for CO and 1.28 $\mu\text{g C/m}^3$ for WSOC, similar to values in the rural air mass R1 that was intercepted near the urban centers along the east coast. It is noted, however, that CO concentrations did reach as low as ~ 70 ppbv (see Figure 5). The background concentrations shown in Figure 6b (CO 121 ppbv, WSOC 0.75 $\mu\text{g C/m}^3$) are used for the remainder of the analysis since in some cases the urban plumes do not have as clear an increase from the background conditions as those in Figure 6, and these are similar to concentrations in the rural air masses measured over the northeastern United States (Table 3 and Figure 2b).

[42] The changes in WSOC concentration relative to CO above background levels (i.e., $\Delta\text{WSOC}/\Delta\text{CO}$) are summarized in Table 4, where the background WSOC and CO was assumed to be the same in all cases. The influence of assuming a constant background concentration on $\Delta\text{WSOC}/\Delta\text{CO}$ is small. For example, on the basis of the standard deviation on what are considered background

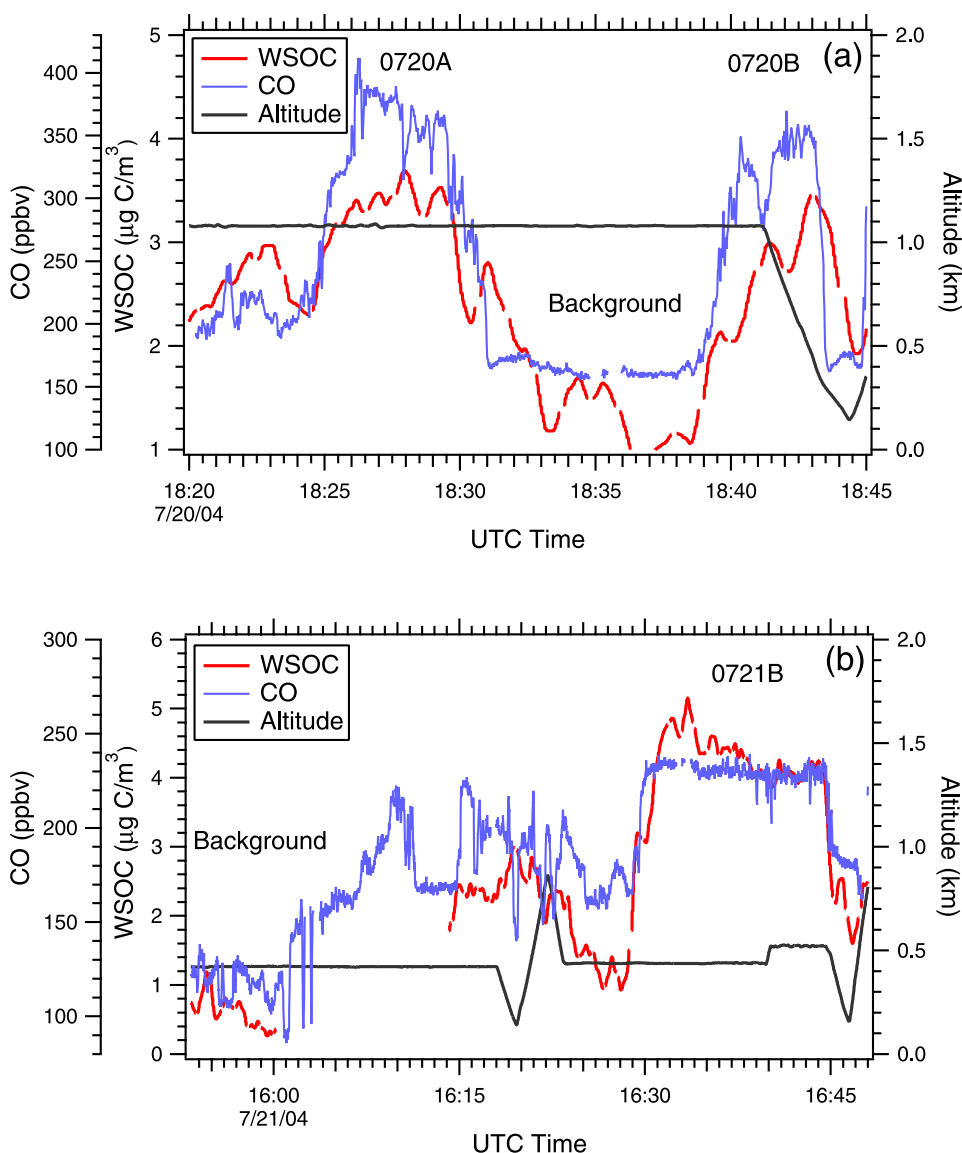


Figure 6. Time series of 3 s WSOC, carbon monoxide, and altitude for (a) two urban plumes intercepted on 20 July 2004 and (b) one urban plume on 21 July 2004 identified in Figure 2c. Local time is EDT = UTC – 4 hours.

concentrations measured at various locations, the variability in $\Delta\text{WSOC}/\Delta\text{CO}$ is $\pm 1.2 \mu\text{g C/m}^3/\text{ppmv}$. The variability in $\Delta\text{WSOC}/\Delta\text{CO}$ given in Table 4 and shown in Figure 7a is the standard deviation of the ratio in the plume, assuming constant background. Variability in the plume is higher than the assumption of constant backgrounds, however, both are relatively small.

[43] On the basis of estimates of plume transport age calculated from the NOAA Air Resources Laboratory (ARL) HYSPLIT trajectory model [Draxler and Rolph, 2003; Rolph, 2003], a general trend in $\Delta\text{WSOC}/\Delta\text{CO}$ is observed. Figure 7a shows $\Delta\text{WSOC}/\Delta\text{CO}$ versus an estimate of the advection time of the plume from the urban region to the measurement site. All plumes were measured

Table 3. WSOC and CO Concentrations in Two Selected Rural Air Masses^a

Air Mass ^b	Measurement Date and UTC Time	WSOC, $\mu\text{g C/m}^3$	CO, ppbv
New England/Canada (R1) ^c	25 Jul 2004, 1430 to 1630, 2055–2130	1.32 (2.13)	133 (177)
Great Lakes/Canada (R2)	6 Aug 2004, 1630–2025	0.85 (1.70)	120 (141)

^aMean concentrations, with maximum in parenthesis, are shown for both air masses. All data have been merged to a 1 min average. Local time is EDT = UTC – 4 hours.

^bFLEXPART and NOAA ARL HYSPLIT trajectory model indicate that the air mass originates from or passed through the given locations within 2 days of the measurement.

^cR1 and R2 are used to identify the rural plumes in Figure 2b.

Table 4. Results for WSOC Evolution in Urban Plumes^a

Plume ID	Measurement Date and UTC Time	Advection Time from Urban Center, ^b hours	Altitude, m	WSOC, $\mu\text{g C/m}^3$	CO, ppbv	$\Delta\text{WSOC}/\Delta\text{CO}$, $\mu\text{g C/m}^3/\text{ppmv}$	WSOC-CO r^2
0720A	20 Jul 2004, 1827–1829	1 \pm 0	1078	3.46 \pm 0.35	362 \pm 21	11.3 \pm 4.1	0.92
0720B	20 Jul 2004, 1840–1842	3 \pm 1	1010	2.59 \pm 0.13	316 \pm 17	8.5 \pm 1.2	0.81
0814A	14 Aug 2004, 1629–1635	13 \pm 1	85	1.08 \pm 0.12	233 \pm 20	3.1 \pm 1.1	0.83
0814A'	14 Aug 2004, 1640–1645	13 \pm 1	86	1.44 \pm 0.45	201 \pm 6	7.2 \pm 5.0	N/A
0814B'	14 Aug 2004, 1921–1929	18 \pm 1	72	2.29 \pm 0.50	195 \pm 14	19.5 \pm 5.0	0.89
0814B	14 Aug 2004, 1931–1936	20 \pm 0	73	3.50 \pm 0.16	249 \pm 17	21.8 \pm 2.7	0.86
0721A	21 Jul 2004, 1517–1529	26 \pm 1	279	4.98 \pm 0.71	272 \pm 27	28.8 \pm 6.8	N/A
0721B	21 Jul 2004, 1629–1643	33 \pm 3	456	4.20 \pm 0.51	227 \pm 11	31.8 \pm 4.1	0.89
0722A	22 Jul 2004, 1834–1850	55 \pm 1	742	3.21 \pm 0.32	199 \pm 9	32.0 \pm 4.1	0.78

^aConcentrations are mean concentrations within the plume based on 3 s data. As an indicator of variability the \pm standard deviation is shown. Local time is EDT = UTC – 4 hours. N/A, not applicable. A background was made either during the rise into or fall out of the plume.

^bCalculated on the basis of the average of NOAA ARL HYSPLIT back trajectories run at the beginning, in the middle, and at the end of each plume.

during the day, however, because some advection times are longer than 1 day, they will include periods of low photochemical activity. Figure 7a shows a number of interesting features. First, for this data set, $\Delta\text{WSOC}/\Delta\text{CO}$ ranged from approximately 3 to 32 $\mu\text{g C/m}^3/\text{ppmv}$. The observations that lowest ratios were generally observed in fresher plumes in measurement regions closer to the urban center, and that these ratios tended to approach zero, suggest that much of the WSOC is a secondary product linked to compounds coemitted with CO (e.g., vehicles). Results from other experiments involving measurements next to vehicle traffic also indicate that this emission ratio should be small. In a more recent study we found that WSOC concentrations measured within ~ 1 m of a major expressway was similar to that measured 400 m away, whereas elemental carbon (EC) was a factor of ~ 7 times larger. Moreover, $\Delta\text{OC}/\Delta\text{CO}$ measured in the Caldecott Tunnel was on the order of ~ 1 $\mu\text{g C/m}^3/\text{ppmv}$ [Kirchstetter *et al.*, 1999] similar to the measurements we recorded closest to the urban centers. In contrast to these fresh plumes, Figure 7a shows that in the more aged and distant plumes from the city, after approximately 1 day of advection time, $\Delta\text{WSOC}/\Delta\text{CO}$ appears to level out approaching a value of about 32 ± 4 $\mu\text{g C/m}^3/\text{ppmv}$, possibly because of a depletion of SOA precursors or other rate-limiting components.

[44] As an interesting contrast to the WSOC behavior, fine particle sulfate (SO_4^{2-}) continued to increase in these regions. For example, plumes 0721A and 0721B also contained significant concentrations of sulfur dioxide (SO_2) and sulfate aerosol, although less evenly distributed throughout the plume than WSOC. For plumes 0721A and 0721B, on average $\Delta\text{SO}_4^{2-}/\Delta\text{CO}$ increased from 89 to 116 $\mu\text{g/m}^3/\text{ppmv}$, respectively (assuming for this simple analysis that background sulfate is zero), whereas $\Delta\text{WSOC}/\Delta\text{CO}$ only increased from 29 to 32 $\mu\text{g C/m}^3/\text{ppmv}$.

[45] For comparison with a previous study in this region, Figure 7a also shows the ΔOC to ΔCO ratio calculated as a function of photochemical age during the NEAQS 2002 experiment [de Gouw *et al.*, 2005]. ($\Delta\text{OC}/\Delta\text{CO}$ was

calculated from the data presented in Figure 14b of de Gouw *et al.* [2005] multiplied by the ratio of acetylene to CO to permit a direct comparison with the results presented in our analysis.) It is noteworthy that our results are consistent with those of de Gouw *et al.* [2005] who employed different measurement techniques and method of analysis.

[46] Formation of SOA and sulfate should lead to increased aerosol volume. Figure 7b shows the ΔPM_1 Volume/ ΔCO for the same plumes in which $\Delta\text{WSOC}/\Delta\text{CO}$ was evaluated and volume data was available. (A constant volume background of $7.15 \mu\text{m}^3/\text{cm}^3$ was assumed and obtained from the background period identified in Figure 6b.) The similar initial increase in volume relative to CO, and similar inflection point at approximately 25 to 30 hours advection time, in Figures 7a and 7b, suggest that the increase in WSOC with plume age was due to gas-to-particle conversion and not solely conversion of primary insoluble OC to WSOC.

4. Summary

[47] A particle-into-liquid sampler coupled with a total organic carbon analyzer (PILS-TOC) was developed for airborne measurements of carbonaceous aerosols that are soluble in water. The instrument was deployed from the NOAA WP-3D aircraft for NEAQS/ITCT 2004 to investigate spatial distributions, sources, and evolution of PM_1 carbonaceous particles over the northeastern United States and Canada, and western portions of the North Atlantic Ocean. WSOC was measured at a 3 s sampling rate. Two main sources for WSOC were identified: biomass burning from long-range transport and emissions from populated regions. Both sources were correlated with CO. No well-defined biogenic sources were observed.

[48] Distinct biomass burning plumes were intercepted between 3 to 4 km altitude over eastern United States and Canada. Back trajectory analysis indicates that all large biomass plumes encountered during the mission were from

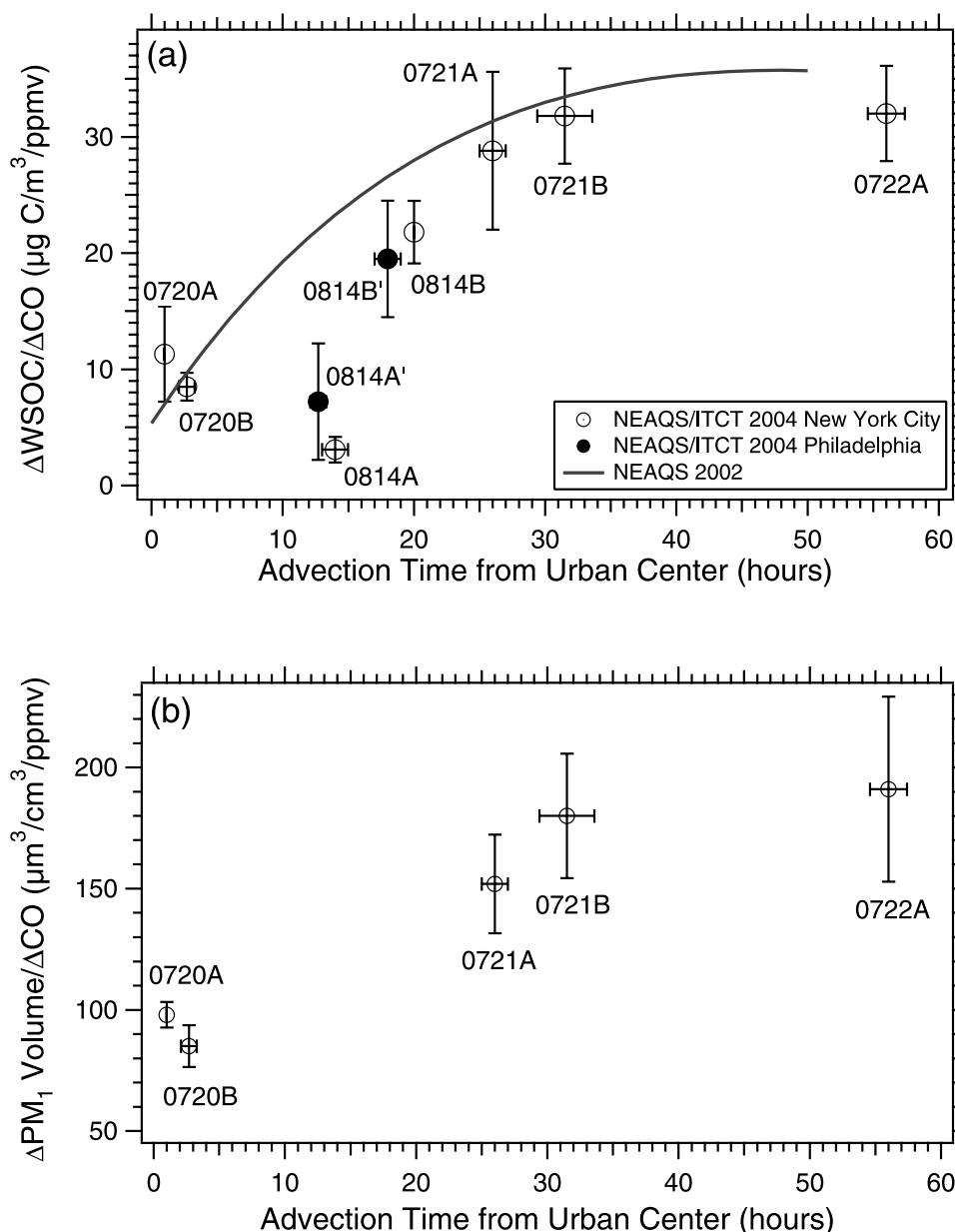


Figure 7. Ratio of (a) ΔWSOC to ΔCO and (b) $\Delta\text{PM}_{1, \text{ Volume}}$ to ΔCO as a function of estimated advection time from the urban center to the measurement site for the plumes identified in Figure 2c and Table 4. The advection time was calculated from the NOAA ARL HYSPLIT trajectory model. On the basis of the FLEXPART model, two of the plumes (solid circles) were likely influenced more by Philadelphia, whereas the other seven (open circles) appear to be influenced primarily by New York City emissions. Uncertainties are the \pm standard deviation of the ratios calculated from variability within the plume (y axis) and of the advection time calculated from variability in back trajectories calculated at the start, in the middle, and at the end of each of the nine plumes (x axis). Included in Figure 7a for comparison is the $\Delta\text{OC}/\Delta\text{CO}$ ratio calculated as a function of photochemical age (solid line) during the NEAQs 2002 study from *de Gouw et al.* [2005]. (Note that units are the same as $\Delta\text{WSOC}/\Delta\text{CO}$.)

fires in the Alaska and northwestern Canada region. WSOC was highly correlated with CO and acetonitrile (r^2 typically >0.88), and the highest fine particle volume and WSOC concentrations were recorded in these plumes.

[49] For air masses not influenced by biomass burning, highest concentrations of WSOC were recorded at lower altitudes, generally below 1000 m, and typically ranged from 2 to 6 $\mu\text{g C}/\text{m}^3$. WSOC showed a rapid concentration

decrease with increasing altitude over the entire measurement domain with concentrations typically less than 1 $\mu\text{g C}/\text{m}^3$ above 3 km. Highest WSOC concentrations were observed in distinct plumes emanating from urban centers. In these plumes WSOC was highly correlated with CO with coefficients of correlation (r^2) larger than 0.78. Rural air masses, which inventories in some cases suggest are associated with significant biogenic emissions, had WSOC

concentrations from the lower detection limit of ~ 0.1 to about $2 \mu\text{g C/m}^3$; significantly less than those measured in urban emissions.

[50] Changes in $\Delta\text{WSOC}/\Delta\text{CO}$ as a function of plume transport time from urban centers showed that the ratio was generally lower ($\sim 3 \mu\text{g C/m}^3/\text{ppmv}$) for fresh plumes, increased with increasing plume age, and leveled off to about $32 \pm 4 \mu\text{g C/m}^3/\text{ppmv}$ (\pm one standard deviation) after approximately 1 day. The data suggests that the production of WSOC associated with PM_{10} particles was strongly linked to compounds coemitted with CO. Concurrent increases in PM_{10} volume suggest that this process rapidly produced significant new mass of secondary aerosol within approximately 1 day. No direct evidence was found for a strong purely biogenic source for PM_{10} WSOC.

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